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Molecular Architecture for Polyphosphazene Electrolytes for Seawater Batteries

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Introduction

Batteries which use seawater not only as the electrolyte but also as the oxidant with inert cathodes have existed for a long time. Among the better examples of these cells are C. L. Optiz's magnesium/steel wool batteries from the late 1960's and M. A. Walsh's Rope Battery. These cells are attractive power sources for a variety of underwater applications as they have a potential for high energy density, moderate cost, and infinite storage properties when kept dry. The difficulty for these systems in seawater is that an adherent calcareous film forms upon them which reduce the current necessary to protect the structure, resulting in cathode performance deterioration. Lithium is particularly attractive as a battery anode material because of its light weight, high voltage, high electrochemical equivalence, and good conductivity. In such a lithium/seawater batteries, lithium serves as the anode and the cathode is the seawater. For lithium, the principal reactions are:

Anode	Li	$- e^-$	$\rightarrow$	Li^+		
Cathode	H_2O	$+ e^-$	$\rightarrow$	OH^-	$+$	$\frac{1}{2}H_2$
Overall	Li	$+ H_2O$	$\rightarrow$	$LiOH$	$+$	$\frac{1}{2}H_2$

However, as apparent from the overall electrochemical reaction, lithium and water will also react directly with one another, essentially resulting in parasitic corrosion of the anode when exposed to water. The corrosion reaction is highly undesirable because it produces no useful electrical energy and consumes active lithium. Further, the reaction is highly exothermic and can have detrimental effects on the battery. Accordingly, the principal challenge with respect to reactive metal-water batteries is development of techniques that minimize this direct lithium-water reaction. Research in liquid electrolytes has typically focused on non-aqueous additives that enhance or result in formation of a calcareous film upon the outer surface of the lithium metal as a means of protecting the metal from direct contact with water. Unfortunately, the use of such non-aqueous liquid electrolytes results in the need for complex battery designs to retain the additives employed within the battery while still affording access to the water to allow the battery to function.

Given this, development of practical lithium/seawater batteries hinges upon developing novel solid polymer electrolytes with the appropriate physical and chemical properties. The membranes paradoxically must allow lithium atoms to pass from the metallic surface, oxidize to the ionic form, and then pass through the membrane to the water outside. At the same time, the membrane must exclude water, tramp ions, and gases such as oxygen and carbon dioxide. Also, the calcareous deposits noted above are avoided due to the presence of the membrane. Recent research at the INL has developed deliberately modified polymer electrolytes based upon the phosphazene family of polymers which have a high probability of addressing the above paradox. Initial studies were performed to determine the impact of molecular architecture within the polyphosphazene structure. The startling magnitude of the differences in electrolyte performance due to molecular architecture is discussed in this paper.

Experimental

Polymer Synthesis. The dichlorophosphazene polymer was made by ring-opening polymerization of phosphonitrilic chloride trimer (Strem) using previously described methods.[1-2] An average of 40-45% conversion to the linear polymer, $(PNCl_2)_n$ was achieved. The organophosphazenes (**1**-**4**) were made using standard literature procedures. A typical synthetic scheme is given here. A solution of was made with toluene. To this was added to a solution of *p*-methoxyphenoxide formed from the reaction of *p*-methoxyphenol and sodium hydride in dry THF. Once added the mixture was stirred for 3 hours. A solution of sodium 2-(2-methoxyethoxy)ethoxide was then prepared via reaction with sodium hydride in dry THF. This solution was then added to the polymer solution followed by heating at 108 °C for 18 hours. Once substitution was complete, the polymer was precipitated into water twice and hexane twice sequentially from THF to obtain a tan colored gum. The MEEP polymer (**1**) was synthesized according to the general procedure above but was isolated and purified in 66% yield via a novel route exploiting the lower critical solubility temperature (LCST) behavior of this material in aqueous solution.[3]

Water Permeation Measurements. The polymer membranes were cast directly on porous supports with an average thickness of 50 μm. These supported membranes were loaded into cells obtained from Millipore and modified for pervaporation experiments. Modification to the Millipore cells consisted of a pumping system to flow feed solution over the membrane at approximately 50 mL/min. A diaphragm vacuum pump capable of providing a transmembrane pressure differential of 550 mmHg was installed on the system with a cryo-trap between the pump and the cell. Permeates were collected for six to eight hours and quantified gravimetrically. Transmembrane fluxes are reported in terms of L/m^2h, where L = volume of permeate, m^2 = membrane area (0.0017 m^2), and h = experimental time.

Electrochemical Measurements. Each polymer was dissolved in dry THF and anhydrous $LiBF_4$ was added to the solution. A range of concentrations was employed, typically from 4 to 10 wt% salt vs polymer weight. Films of the salted polymers were cast directly on SS316 steel electrodes measuring 1.00 cm^2 and dried in a vacuum/Argon oven for several hours. A second steel electrode was placed on top of the films and impedance measurements were taken with a PARC model 273A potentiostat coupled to a Solartron SI 1260 impedance/gain-phase analyzer, with computer control provided by Z-plot for Windows (Scribner Assoc.). A frequency sweep technique was employed with a range of 10kHz to 1Hz. Conductivity reported is for the salt loading level that exhibited maximum conductivity for each individual polymer.

Results and Discussion

In formulating polymer electrolytes for seawater battery applications, the material must both conduct lithium ions as well as minimize water permeation. For polyphosphazenes, this requirement is met by incorporating some pendant groups that impart a hydrophobic nature along with some pendant groups that are highly polar to afford lithium ion conduction. How to best incorporate both of these opposing groups into one polymer was a question of molecular architecture that was the subject of our investigations. Since organophosphazenes can be considered to have three principal components – the backbone, the hydrophobic region and the conductive region. Three alternate molecular architectures result from this situation. The first of these architectures is to form a homopolymer from a single pendant group that incorporates both components. Groups of this type are readily commercially available as non-ionic surfactants. However, with this design, one has the choice of connecting the surfactant moiety to the phosphazene

backbone either through the hydrophobic portion, resulting in a core of hydrophobicity and a conductive region that is shifted away from the backbone; or through the conductive portion, resulting in a backbone centered ion channel surrounded by a hydrophobic sheath. Representatives of both molecular architectures were synthesized and are shown in Figures 1 and 2.

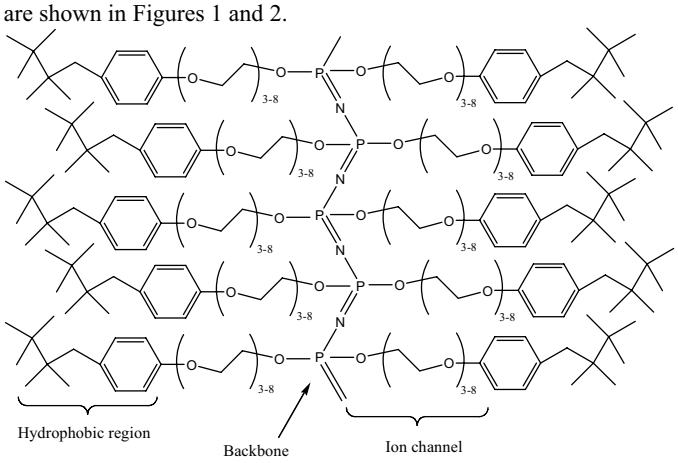

Figure 1. Structure of the triton polymer. This electrolyte possesses the correct molecular architecture to maximize ion conduction.

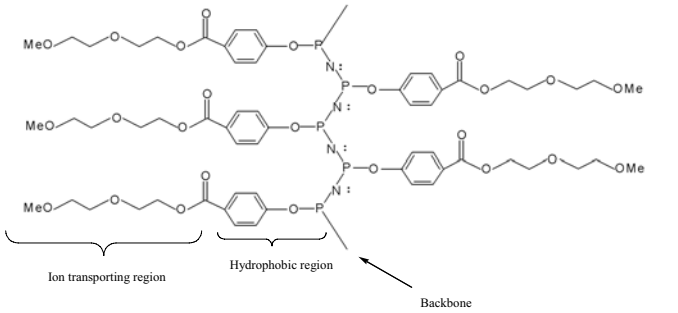

Figure 2. Structure of the DEG ester polymer. In this molecular architecture, the ion channel is "shifted" away from the backbone, resulting in the poorest conductivity.

The third choice for molecular architecture is to form a simple heteropolymer by mixing to different pendant groups – one polar and one hydrophobic. To complete our series for evaluation, a representative of this molecular architecture was prepared as well as shown in Figure 3.

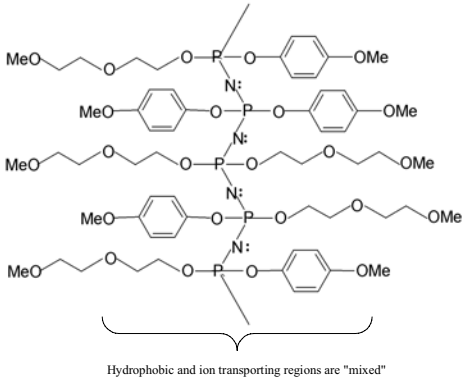

Figure 3. Structure of the 50/50 polymer. In this molecular architecture, the ion channel is "clogged" leading to reduced conductivity.

The water permeability and lithium ion conductivity were measured for these three representative polymers and the results are given in Tables 1 and 2. The well-studied MEEP polymer was also evaluated as a benchmark. As shown in Table 1, the water permeabilities for the three molecular architectures were very similar. This is attributed to the fact the ratio of hydrophobic portion to the conductive portion was very similar for all three polymers, and water transport can be understood to be reflective of this ratio. However, the ionic conductivity of the three polymers was very different – different by a factor of over 15,000. This is explained through the impact of molecular architecture. The mechanism of lithium ion conduction is dependant on a key role played by the nitrogen atoms in phosphazene backbone. This backbone assisted transport mechanism (BIM) affords much more facile ion transport than that via other possible transport mechanisms, such as a hand-to-hand mechanism. As a consequence, when the conductive region is centered on the backbone, the BIM becomes dominant and conductivity is markedly increased. When the conductive region is remote from the backbone, other transport mechanisms dominate and conductivity is lower. In the intermediate architecture, some of the conductive region is near the backbone, but there is no clear all-conductive region – resulting in an ion channel that is "clogged" by hydrophobic moieties. In this instance some BIM transport is possible, but other mechanisms must be responsible for moving through/around the hydrophobic portions. This mixed transport situation leads, logically, to an intermediate conductivity.

Table 1. Water Permeability of Polymer Electrolytes

Polymer Tested	Water Flux (L/M^2*h)
MEEP (**1**)	Dissolves readily
Triton (**2**)	0.013
50/50 DEG/MeOP (**3**)	0.011
DEG Ester (**4**)	0.040

Table 2. Conductivity of Polymer Electrolytes

Polymer Tested	Conductivity (nS/cm)
MEEP (**1**)	43,000
Triton (**2**)	850
50/50 DEG/MeOP (**3**)	41
DEG Ester (**4**)	0.054

Conclusions

Through this work, we have demonstrated that the molecular architecture within the polyphosphazene is critical to performance as an electrolyte membrane suitable for lithium seawater batteries.[4] From these studies, the backbone centered ion channel (BIM) mechanism of lithium transport was developed. Further studies have since confirmed this lithium transport mechanism[5], so all future polyphosphazenes for seawater battery applications will posses this correct molecular architecture.

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References

(1) Allcock, H. R., *Phosphorous-Nitrogen Compounds*, Academic Press, New York, **1972**.
(2) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L.; Polym. Sci. Eng.**1975**, *15(5)*, 321.
(3) Harrup, M. K.; Stewart, F. F.; J. Appl. Poly. Sci., **2000**, *78(5)*, 1092.
(4) Harrup, M. K.; Stewart, F. F.; Peterson, E. S. *U. S. Patent # 6,146,787*, November 14, **2000**.
(5) Luther, T. A.; Stewart, F. F.; Budzien, J. L.; LaViolette, R. A.; Bauer, W. F.; Harrup, M. K.; Allen, C. W.; Elayan, A.; *Journal of Physical Chemistry B*, **2003**, *107*, 3168-3176.